Predicting spinel solid solutions using a random atom substitution method

Supplementary Information

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1 Supplementary Note 1 - ChemDASH stages

An initial structure is defined either from a cif file or constructed from a set of grid points and the initial structure is relaxed to a local energy minimum. Local energy minimisation of each structure is performed by external structure optimisation codes. Currently supported are the force-field code GULP[1] and the periodic density functional theory (DFT) code VASP.[2] The total energy of the system after relaxation is then used in the acceptance criteria.

Ranking of atoms can be performed in ChemDASH by three separate methods: random, bond valence sum (BVS) and electrostatic potential. The BVS method is implemented such that the deviation of each atom from its ideal BVS (derived from experiment[3–5]) is calculated. This is the ranking criterion used throughout this work. This ranking then generates a list for atoms to be prioritised for swapping. Once a list of atoms is generated, the possible swap groups are determined and a weighting scheme determines the number of atoms to be swapped. This weighting is biased towards swapping fewer atoms. Swap groups can be customised for any given atom pair or the more general defaults swapping cations, anions and/or vacancies can be specified.

The Metropolis criterion[6] is used (after structural relaxation and total energy calculation of the structure) to determine if a swap should be accepted or rejected. The energy difference ΔE between the current and the previous structure is used in the Metropolis criterion as:

$$R < \exp\left(\frac{-\Delta E}{k_B T}\right) \tag{1}$$

where R is a random number between 0 and 1 generated at each ChemDASH step, k_B is the Boltzmann constant and T the temperature. Swaps which reduce the energy of the system (relative to the previous structure) are always accepted whereas swaps that increase the energy are accepted with an exponentially decaying probability as the energy difference increases. The value of $k_B T$ can be specified to allow for higher/lower temperatures to be modelled and therefore will increase/decrease the probability of acceptance. Accepted structures are then used as the new starting structure for the next ChemDASH swap.

References

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[4] I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B*, 1985, **41**, 244–247.

[5] N. E. Brese and M. O'Keeffe, *Acta Crystallogr. Sect. B*, 1991, **47**, 192–197.

[6] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller, *Cit. J. Chem. Phys*, 1953, **21**, 1087.

Supplementary Figures and Tables
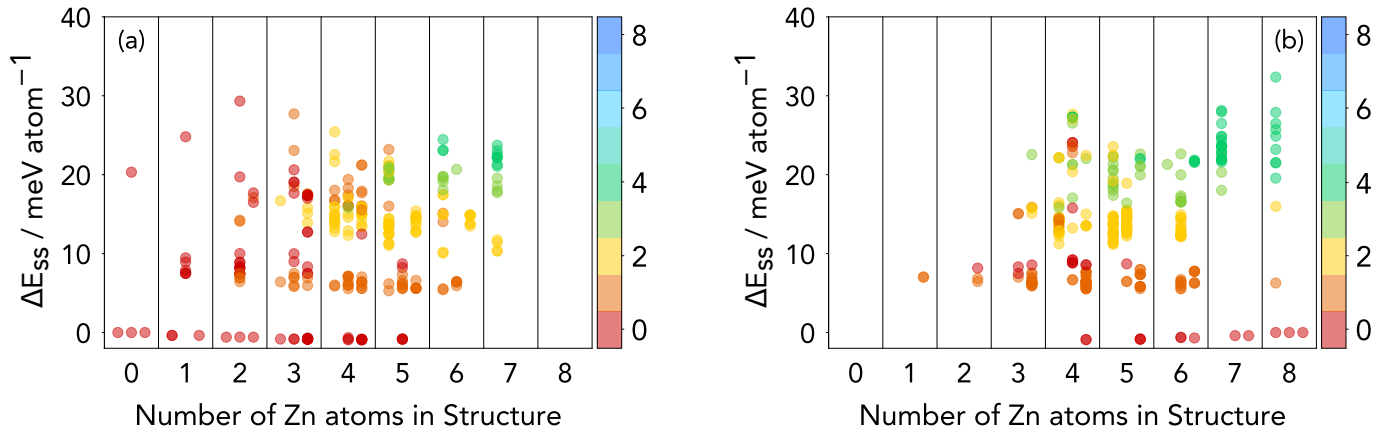
Supplementary Figure 1: Distribution of structure energies for ChemDASH runs starting at normal (a) MnFe$_2$O$_4$ and (b) ZnFe$_2$O$_4$ with the FiM magnetic structure as a function of the number of Zn atoms in the structure. Runs with 25% (left), 50% (central) and 75% (right) are plotted and each run is coloured by the number of Zn atoms in octahedral sites to show the evolution of each ChemDASH run. ΔE_{ss} is defined relative to the energies of FiM normal MnFe$_2$O$_4$ and FiM normal ZnFe$_2$O$_4$.
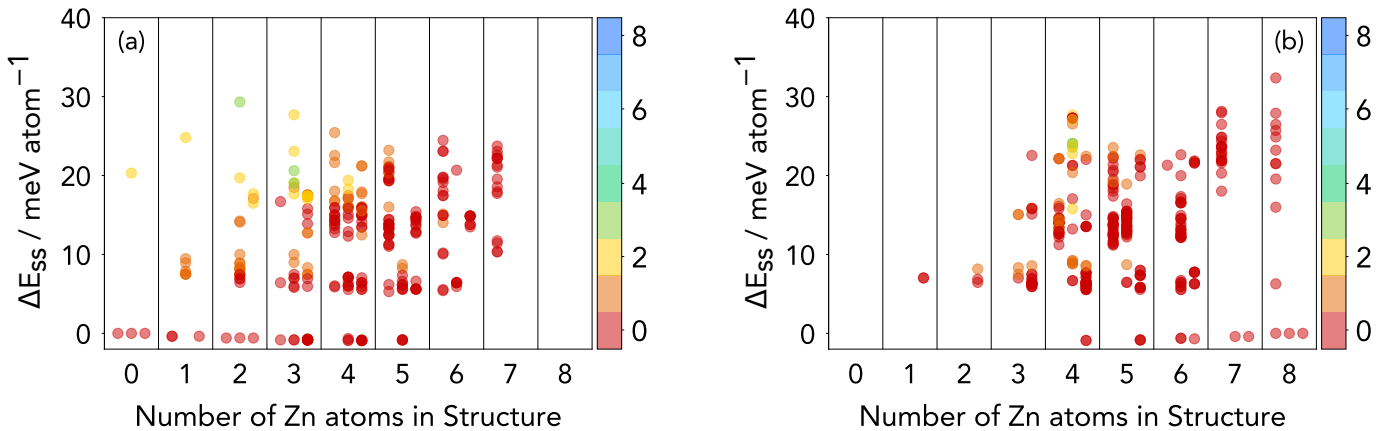
Supplementary Figure 2: Distribution of structure energies for ChemDASH runs starting at normal (a) MnFe$_2$O$_4$ and (b) ZnFe$_2$O$_4$ with the FiM magnetic structure as a function of the number of Zn atoms in the structure. Runs with 25% (left), 50% (central) and 75% (right) are plotted and each run is coloured by the number of Mn atoms in octahedral sites to show the evolution of each ChemDASH run. ΔE_{ss} is defined relative to the energies of FiM normal MnFe$_2$O$_4$ and FiM normal ZnFe$_2$O$_4$.

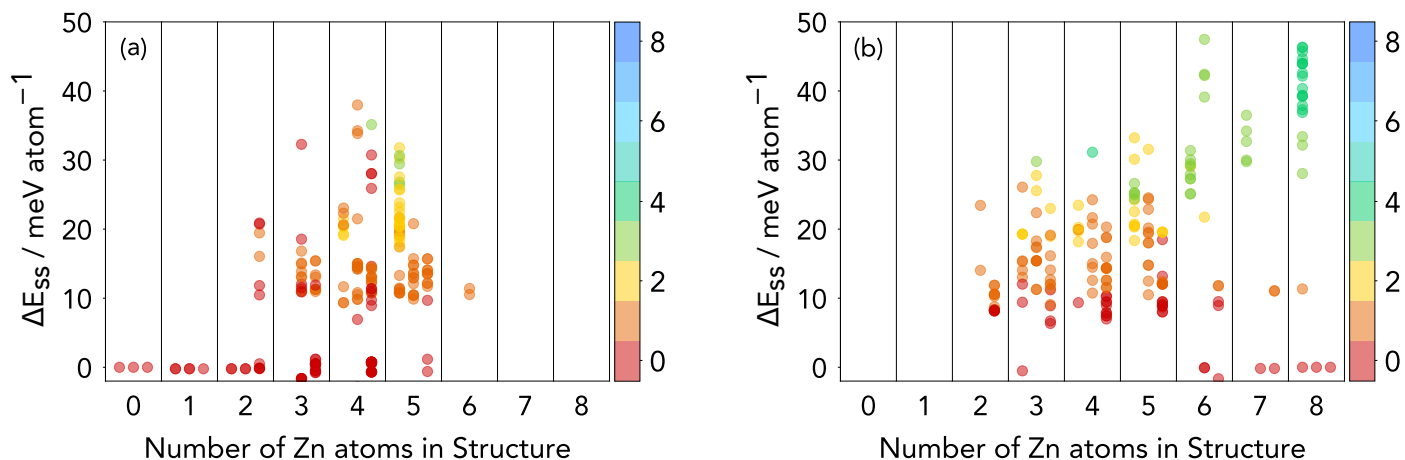Supplementary Figure 3: Distribution of structure energies for ChemDASH runs starting at normal (a) $MnFe_2O_4$ and (b) $ZnFe_2O_4$ with the AFM magnetic structure as a function of the number of Zn atoms in the structure. Runs with 25% (left), 50% (central) and 75% (right) are plotted and each run is coloured by the number of Mn atoms in octahedral sites to show the evolution of each ChemDASH run. ΔE_{ss} is defined relative to the energies of AFM normal $MnFe_2O_4$ and AFM normal $ZnFe_2O_4$.

Convex Hull Species	E_{hull} / meV atom^{-1}	Note
O_2	0.00	
Fe_1	0.00	
Mn_{29}	0.00	
Zn_2	0.00	
Zn_3	4.61	
Fe_4O_4	0.00	
Fe_4O_6	0.00	
Fe_6O_8	0.00	
Mn_2O_2	0.00	
Mn_4O_8	0.00	
Mn_5O_8	6.54	
Mn_6O_8	0.00	
$Mn_{32}O_{48}$	0.00	
Zn_2O_2	0.00	
$Mn_2Fe_4O_8$	0.00	Normal Spinel
$Mn_2Fe_4O_8$	43.92	Inverse Spinel
$Mn_8Fe_8O_{24}$	33.83	
$Mn_4Fe_2O_8$	10.00	
$Mn_2Zn_2O_6$	0.00	
$Mn_4Zn_2O_8$	0.00	
$Mn_4Zn_{16}O_{20}$	0.00	
$Mn_3Zn_2O_8$	0.00	
$Mn_6Zn_2O_{14}$	0.12	
$Zn_2Fe_4O_8$	0.00	
$Zn_{11}Fe_{25}O_{48}$	12.93	
$Zn_1Mn_7Fe_{16}O_{32}$	0.00	FiM ordering
$Zn_2Mn_6Fe_{16}O_{32}$	0.13	FiM ordering
$Zn_3Mn_5Fe_{16}O_{32}$	0.39	FiM ordering
$Zn_4Mn_4Fe_{16}O_{32}$	0.73	FiM ordering
$Zn_5Mn_3Fe_{16}O_{32}$	1.23	FiM ordering
$Zn_6Mn_2Fe_{16}O_{32}$	1.81	FiM ordering
$Zn_7Mn_1Fe_{16}O_{32}$	0.53	AFM ordering

Supplementary Table 1: Convex hull species and energies for all known stable phases in the Mn-Fe-Zn-O phase field. Calculations were conducted with a k-point spacing of 0.16 Å^{-1}.
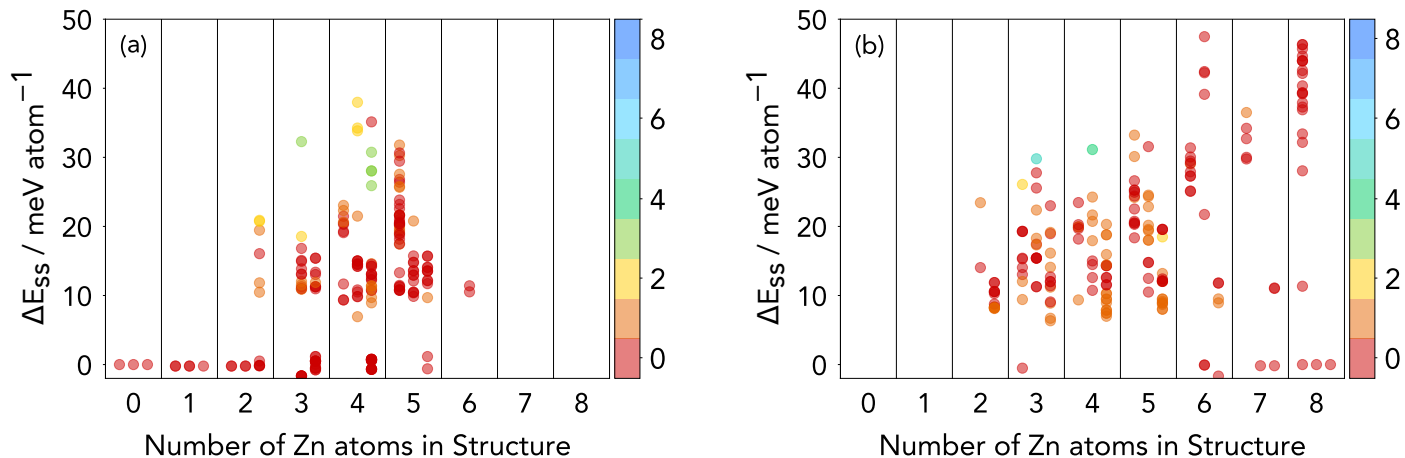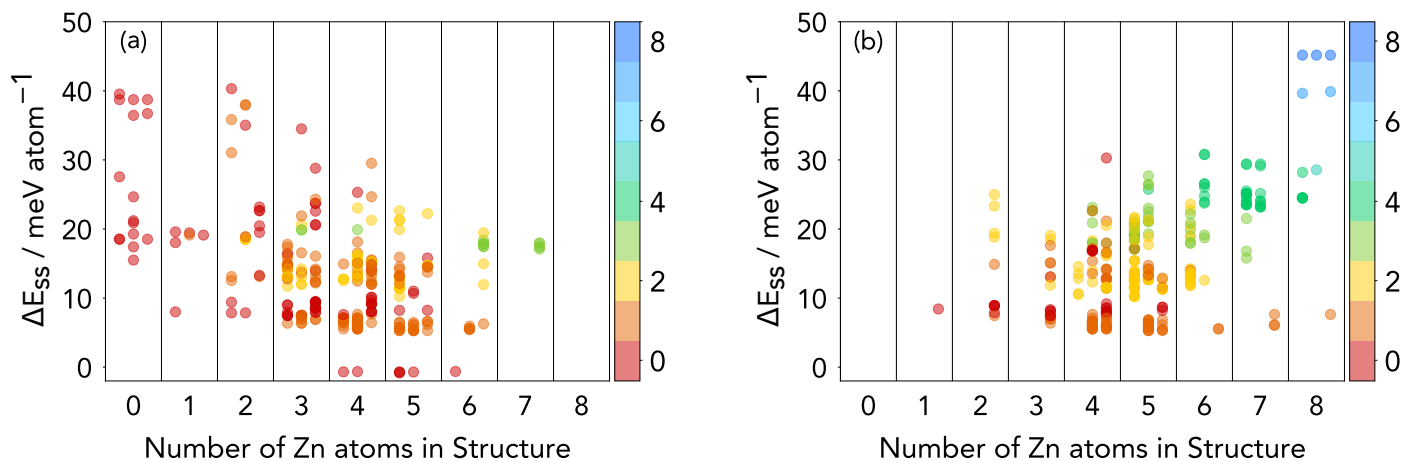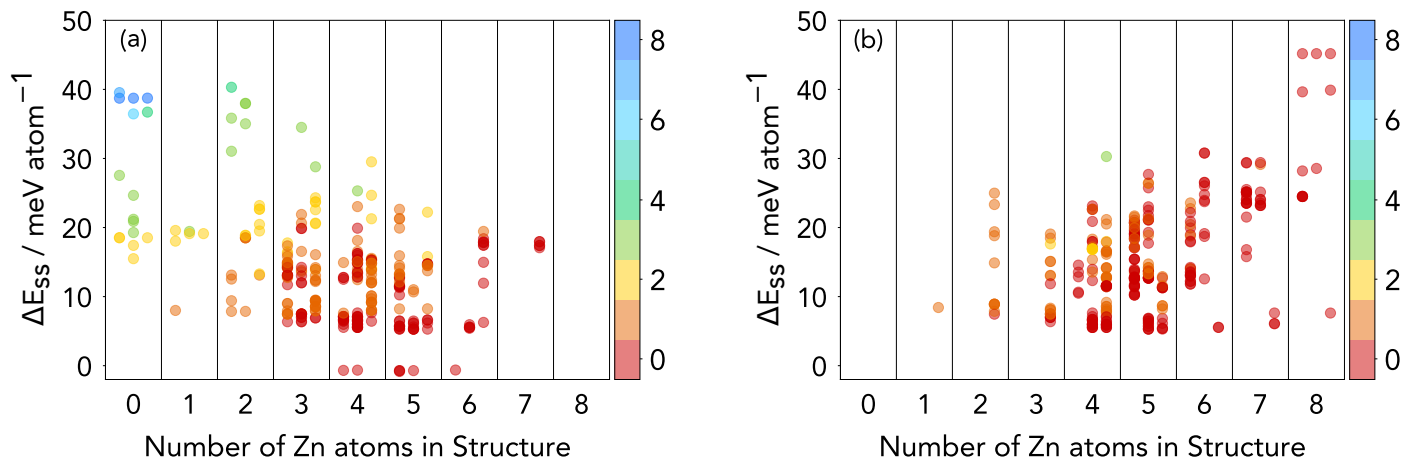
Supplementary Figure 4: Distribution of structure energies for ChemDASH runs starting at normal (a) $MnFe_2O_4$ and (b) $ZnFe_2O_4$ with the AFM magnetic structure as a function of the number of Mn atoms in the structure. Runs with 25% (left), 50% (central) and 75% (right) are plotted and each run is coloured by the number of Mn atoms in octahedral sites to show the evolution of each ChemDASH run. ΔE_{ss} is defined relative to the energies of AFM normal $MnFe_2O_4$ and AFM normal $ZnFe_2O_4$.

Supplementary Figure 5: Distribution of structure energies for ChemDASH runs starting at inverse (a) $MnFe_2O_4$ and (b) $ZnFe_2O_4$ with the FiM magnetic structure as a function of the number of Zn atoms in the structure. Runs with 25% (left), 50% (central) and 75% (right) are plotted and each run is coloured by the number of Mn atoms in octahedral sites to show the evolution of each ChemDASH run. ΔE_{ss} is defined relative to the energies of FiM normal $MnFe_2O_4$ and FiM normal $ZnFe_2O_4$.

Supplementary Figure 6: Distribution of structure energies for ChemDASH runs starting at inverse (a) $MnFe_2O_4$ and (b) $ZnFe_2O_4$ with the FiM magnetic structure as a function of the number of Mn atoms in the structure. Runs with 25% (left), 50% (central) and 75% (right) are plotted and each run is coloured by the number of Mn atoms in octahedral sites to show the evolution of each ChemDASH run. ΔE_{ss} is defined relative to the energies of FiM normal $MnFe_2O_4$ and FiM normal $ZnFe_2O_4$.
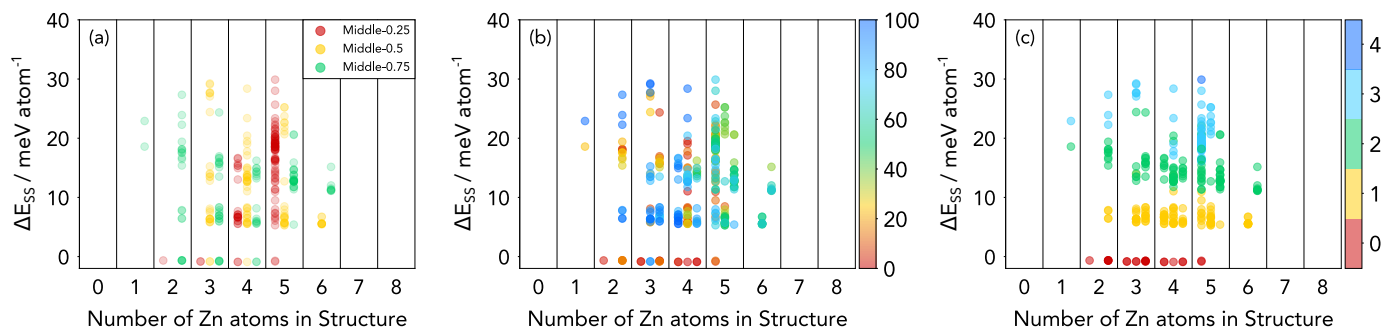

Supplementary Figure 7: Distribution of structure energies for ChemDASH runs starting at Normal $Mn_4Zn_4Fe_{16}O_{32}$ with the FiM magnetic structure as a function of the number of Mn atoms in the structure. Runs with 25% (left), 50% (central) and 75% (right) are plotted and each run is coloured by the number of Mn atoms in octahedral sites (a), the structure index (b) and the number of Fe atoms in tetrahedral sites (c) to show the evolution of each ChemDASH run. ΔE_{ss} is defined relative to the energies of FiM normal $MnFe_2O_4$ and FiM normal $ZnFe_2O_4$.

Starting Structure	Cationic Ordering	Magnetic Structure	Substitution Rate %	Total Acceptance Rate %	Doping Acceptance Rate %	Swapping Acceptance Rate %
$MnFe_2O_4$	Normal	FiM	25	81.2	53.3	94.3
			50	75.0	58.0	90.0
			75	59.2	50.7	92.6
		AFM	25	80.0	47.8	87.7
			50	73.0	57.4	89.1
			75	62.9	58.7	84.0
$MnFe_2O_4$	Inverse	FiM	25	81.3	58.1	88.4
			50	72.1	50.0	86.5
			75	55.5	41.8	90.5
		AFM	25	86.7	68.0	90.7
			50	61.4	21.4	91.4
			75	42.1	28.8	85.2
$ZnFe_2O_4$	Normal	FiM	25	84.2	52.0	98.7
			50	71.6	41.5	91.5
			75	63.3	62.2	73.1
		AFM	25	79.0	29.2	94.7
			50	59.0	33.3	87.8
			75	60.6	59.0	86.4
$ZnFe_2O_4$	Normal	FiM	25	87.1	53.8	98.7
			50	77.7	50.0	96.4
			75	61.2	57.7	86.4
		AFM	25	68.8	35.0	86.3
			50	56.4	17.6	87.8
			75	50.6	24.1	90.5

Supplementary Table 2: Table of acceptance rates for each vc-ChemDASH run